

Emerging Issues in Lake St. Clair

Introduction:

The term "emerging issues" refers to the study of environmental pollutants that have been discovered and intensively studied only in the last five years [1]. For this study, we chose to concentrate on three classes of emerging contaminants, Polybrominated diphenyl ethers (PBDEs), perfluorooctane sulfonate (PFOS), and polychlorinated naphthalenes (PCNs).

The general structure of PBDEs is shown in Figure 1. PBDEs have varying degrees of bromination. The congeners (one of the many variants of a common chemical structure) are numbered from 1 to 209 using the same IUPAC (International Union of Pure and Applied Chemistry) scheme used for polychlorinated biphenyls (PCBs) [2].

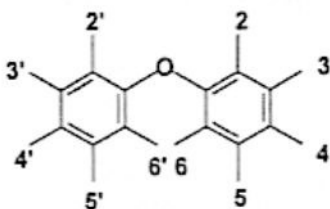


Figure 1. General structure of PBDEs; $C_{12}OBr_xH_{(10-x)}$. The positions 2-6 and 2'-6' may contain either bromine or hydrogen atoms. In theory, 209 different molecules are possible [3].

The structure of PFOS anion is shown in Figure 2. The figure shown is that of the potassium salt.

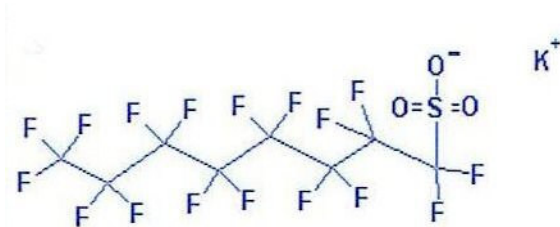


Figure 2. Potassium perfluorooctane sulphonate (CAS No. 2795-39-3) [4]

PCNs are a group of 75 theoretically possible chlorinated naphthalenes, general chemical formula $C_{10}H_{(8-n)}Cl_n$, containing one to eight chlorine atoms bound to the naphthalene di-benzene ring [5].

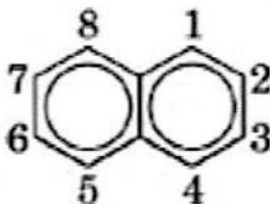


Figure 3. Structure and naming convention for the polychlorinated naphthalenes [5].

Figure 4 shows an example of a commercial polychlorinated naphthalene.

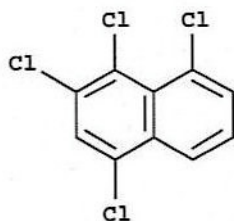


Figure 4. 1,2,4,8-tetrachloronaphthalene (CAS 6529-87-9) [5]

Polybrominated diphenyl ethers (PBDEs) are an important class of brominated fire-retardants [6]. Brominated flame-retardants are added to many plastics, textiles, and polyurethane foam padding used in furniture and carpets [7]. Recent evidence has confirmed that PBDEs are ubiquitous contaminants present in all ecosystems at concentrations up to the part-per-million range. In industrialized and pristine regions of North America, PBDE concentrations are increasing rapidly at rates which may be more rapid than was ever observed for PCBs [8]. PBDEs have been shown to bioconcentrate in the tissues of fish. Catfish taken from the Detroit River were found to have a concentration of 21,069 pg/g total PBDE in their blood plasma [6].

Perfluorooctane sulfonate (PFOS) salts are fully fluorinated organic compounds that can be produced synthetically or through the degradation of other perfluorochemical products. Sulfonyl-based perfluoroalkylated compounds have been produced and used for over 40 years for soil/stain resistance and surfactant applications. Recent studies have shown that PFOS is a persistent and bioaccumulative global contaminant [10]. The major suspected sources of PFOS and other perfluorochemicals are releases through aqueous industrial and residential wastestreams [12]. The 3M company announced the phase out of the production of PFOS-based chemicals in December, 2000, because of concerns about the persistence of PFOS in the environment and the potential for long-term environmental effects [10,12].

Polychlorinated naphthalenes (PCNs) have been known for about 170 years and have been commercially produced and used for about 100 years [13]. They were used in engine oil additives and other lubricants, wood preservatives and moisture proofing sealants, cable insulation and capacitor fluids, and for flame proofing and electroplating purposes. The lower chlorinated PCN mixtures were used predominantly as lubricants whereas the higher chlorinated mixtures were used for capacitor impregnation and electrical insulation. Commercial production of these mixtures ceased in 1980 [5].

Study Design:

In the present study, a total of six sediment samples, five aqueous samples, and two fish homogenates were prepared for PBDE, PFOS and PCN analysis. One of the two fish homogenates was composed of three carp (a benthic feeder) and the other was composed of four northern pike (a pelagic feeder).

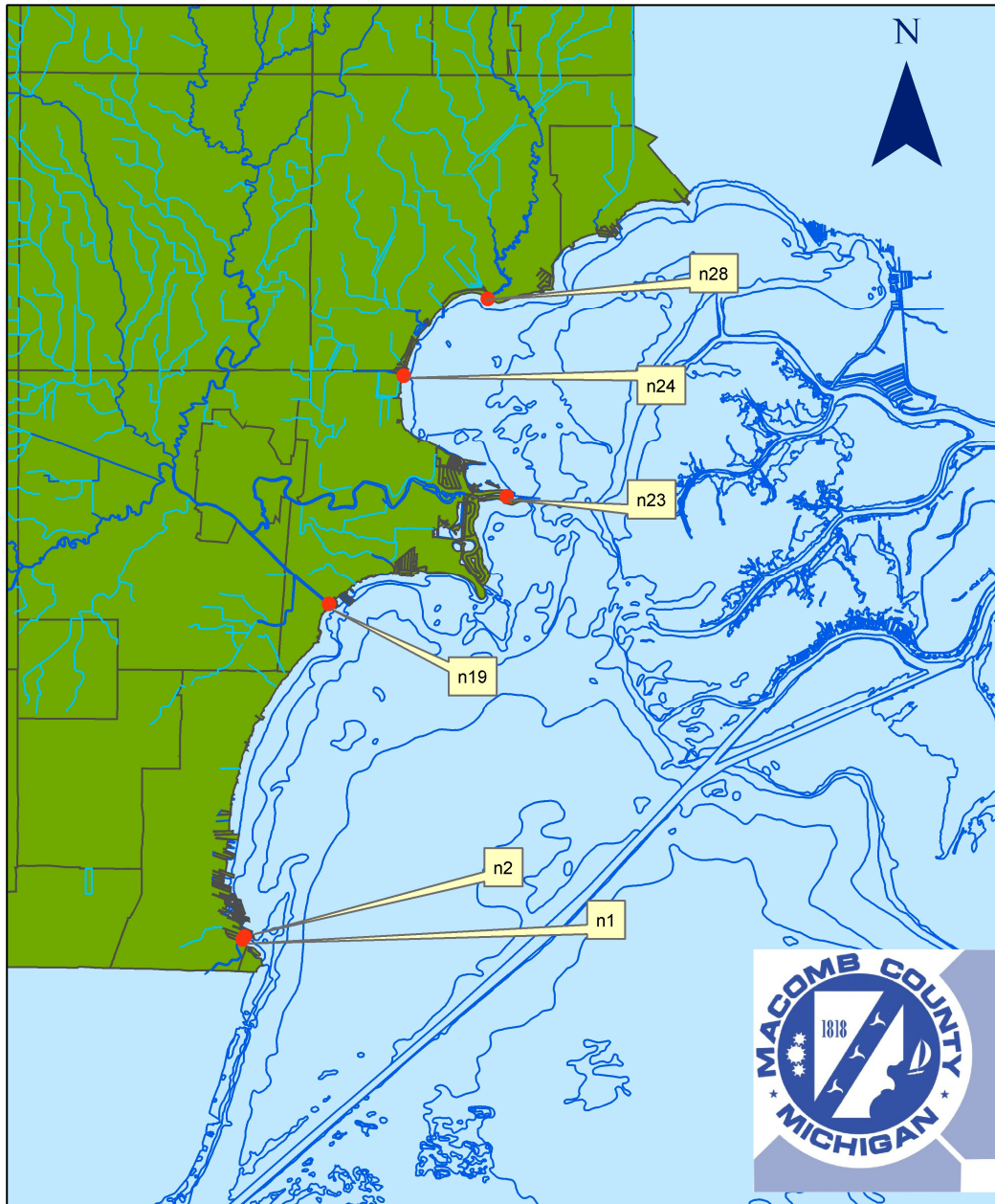
The samples were collected at six near shore sampling sites in Lake St. Clair. The sites were selected through a review of historic Macomb County Health Department Lake St. Clair Assessment data. They were selected because of sediment quality problems with nutrients, metals, pesticides and/or other organic contaminants. The sites included the Milk River [n1], Liberty Drain [n2], Clinton River Spillway [n19], Clinton River [n23], Irwin Drain [n24], and Salt River [n28] [Figure 5]. All sample locations are at the outfalls to Lake St. Clair. The fish samples were provided by the Michigan Department of Environmental Quality.

Methods:

Sample collection procedures and laboratory analytical procedures are described in the project's quality assurance project plan.

Figure 5.

Emerging Issues Project Sample Sites



Results and Discussion:

No polychlorinated naphthalenes were found in any aqueous, sediment, or fish tissue sample taken for this project. The detection limits are given in Table 1.

Table 1.
Polychlorinated Naphthalenes
Aqueous Sample Results

	n1	n19	n23	n24	n28
Monochloronaphthalene, Total	U	U	U	U	U
Dichloronaphthalene, Total	U	U	U	U	U
Trichloronaphthalene, Total	U	U	U	U	U
Tetrachloronaphthalene, Total	U	U	U	U	U
Pentachloronaphthalene, Total	U	U	U	U	U
Hexachloronaphthalene, Total	U	U	U	U	U
Heptachloronaphthalene, Total	U	U	U	U	U
Octachloronaphthalene, Total	U	U	U	U	U
Detection limit (µg/L):	0.98	0.94	0.97	0.96	0.97

Sediment Sample Results

	n1	n2	n19	n23	n24	n28
Monochloronaphthalene, Total	U	U	U	U	U	U
Dichloronaphthalene, Total	U	U	U	U	U	U
Trichloronaphthalene, Total	U	U	U	U	U	U
Tetrachloronaphthalene, Total	U	U	U	U	U	U
Pentachloronaphthalene, Total	U	U	U	U	U	U
Hexachloronaphthalene, Total	U	U	U	U	U	U
Heptachloronaphthalene, Total	U	U	U	U	U	U
Octachloronaphthalene, Total	U	U	U	U	U	U
Detection limit (µg/kg):	71	59	51	59	77	81

Fish Tissue Results

	Carp	Northern Pike
Monochloronaphthalene, Total	U	U
Dichloronaphthalene, Total	U	U
Trichloronaphthalene, Total	U	U
Tetrachloronaphthalene, Total	U	U
Pentachloronaphthalene, Total	U	U
Hexachloronaphthalene, Total	U	U
Heptachloronaphthalene, Total	U	U
Octachloronaphthalene, Total	U	U
Detection limit (µg/kg):	160	33

U: Undetected

No Perfluorooctane sulfonate was found in any aqueous or sediment sample taken for this project. The detection limits are given in Table 2.

Perfluorooctane sulfonate was found in fish tissue homogenate obtained from both Carp and Northern Pike. The PFOS concentration found in the Carp homogenate was 4.40 ng/g, and the PFOS concentration found in the Northern Pike homogenate was 41.2 ng/g. These results appear in Table 2.

Table 2.
Perfluorooctane Sulfonate
Aqueous Sample Results

n1	n19	n23	n24	n28
U	U	U	U	U

Detection Limit: 50 ng/L

Sediment Sample Results

	n1	n2	n19	n23	n24	n28
Perfluorooctane Sulfonate	U	U	U	U	U	U
Detection limit (ng/kg):	0.474	0.369	0.273	0.368	0.553	0.383

Fish Tissue Results

	Carp	Northern Pike
Perfluorooctane Sulfonate (ng/g)	4.40	41.2

U: Undetected

The PBDE results include the predominant congeners found in a 2001 study of Lake Michigan salmonids and commercial mixtures of PBDEs [14]. The congeners include: 2,4,4'-tribromodiphenyl ether; 2,2', 4,4', 5,5'-hexabromodiphenyl ether; 2,2', 4,4'-tetrabromodiphenyl ether; 2,2', 4,4', 5,6'-hexabromodiphenyl ether; 2,2', 4,4', 5-pentabromodiphenyl ether; 2,2', 3,4,4', 5', 6-heptabromodiphenyl ether; 2,2', 4,4', 6-pentabromodiphenyl ether; and decabromodiphenyl ether.

Polybrominated diphenyl ethers were found in all aqueous, sediment, and fish homogenate samples tested except for the sediment sample taken from the Clinton River site (n23). These results are found in Table 3.

Table 3a.
Polybrominated Diphenyl Ethers
Aqueous Sample Results

PBDE Congener #	Detection limit (pg/L)	n1	n19	n23	n24	n28
28	100	U	U	U	U	U
47	2000	U	U	U	U	U
66	100	U	U	U	U	U
85	120	U	U	U	U	U
99	2000	U	U	U	U	U
100	100	270	U	U	140	130
138	100	U	U	U	U	U
153	120	580	670	U	220	U
154	100	190	160	450	U	U
183	100	2500	3400	U	850	200
209	20000	U	U	U	22000	U
Σ PBDEs		3540	4230	450	23210	330

Fish Tissue Results

PBDE Congener #	Carp		Northern Pike	
	Result (pg/g)	DL (pg/g)	Result (pg/g)	DL (pg/g)
28	300	10	220	10
47	3300	500	11000	500
66	U	10	160	10
85	U	12	U	12
99	U	500	3800	500
100	540	100	2400	100
138	U	100	U	100
153	U	12	570	12
154	210	10	680	10
183	U	10	13	10
209	U	5000	U	5000
Σ PBDEs	4350		18843	

U: Undetected

DL: Detection Limit

Table 3b.
Polybrominated Diphenyl Ethers
Sediment Sample Results

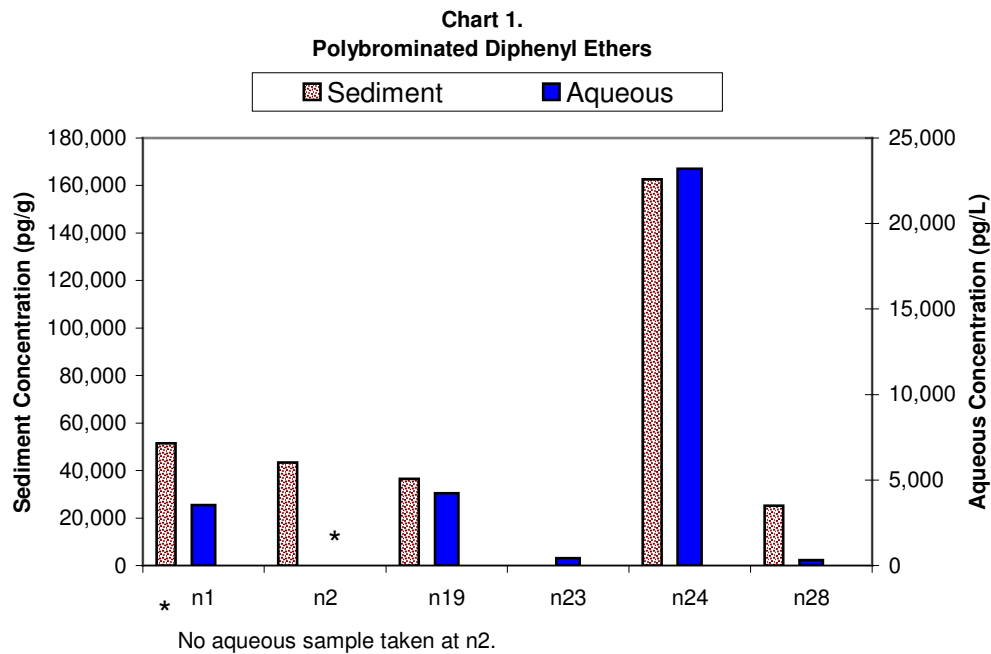
PBDE Congener #	n1		n2		n19	
	Result (pg/g)	DL (pg/g)	Result (pg/g)	DL (pg/g)	Result (pg/g)	DL (pg/g)
28	110	23	64	18	38	18
47	3500	1100	1700	900	880	900
66	120	23	72	18	39	18
85	120	27	55	22	32	22
99	3800	1100	1700	900	940	900
100	890	230	420	180	240	180
138	U	230	U	180	U	180
153	430	27	200	22	110	22
154	360	23	190	18	130	18
183	140	23	59	18	85	18
209	42000	11000	39000	9000	34000	9000
Σ PBDEs	51470		43460		36494	

PBDE Congener #	n23		n24		n28	
	Result (pg/g)	DL (pg/g)	Result (pg/g)	DL (pg/g)	Result (pg/g)	DL (pg/g)
28	U	16	48	27	58	24
47	U	810	U	1400	U	1200
66	U	16	53	27	37	24
85	U	19	51	33	30	29
99	U	810	1300	1400	U	1200
100	U	160	310	270	U	240
138	U	160	U	270	U	240
153	U	19	250	33	94	29
154	U	16	190	27	83	24
183	U	16	400	27	42	24
209	U	8100	160000	14000	25000	12000
Σ PBDEs	U		162602		25344	

U: Undetected
DL: Detection Limit

The highest concentration of PBDEs, in both aqueous and sediment samples, occurred at Irwin Drain (n24). The total aqueous PBDE concentration was 23210 pg/L, more than four times the next highest total aqueous PBDE concentration, 4230 pg/L, at Clinton River Spillway (n19).

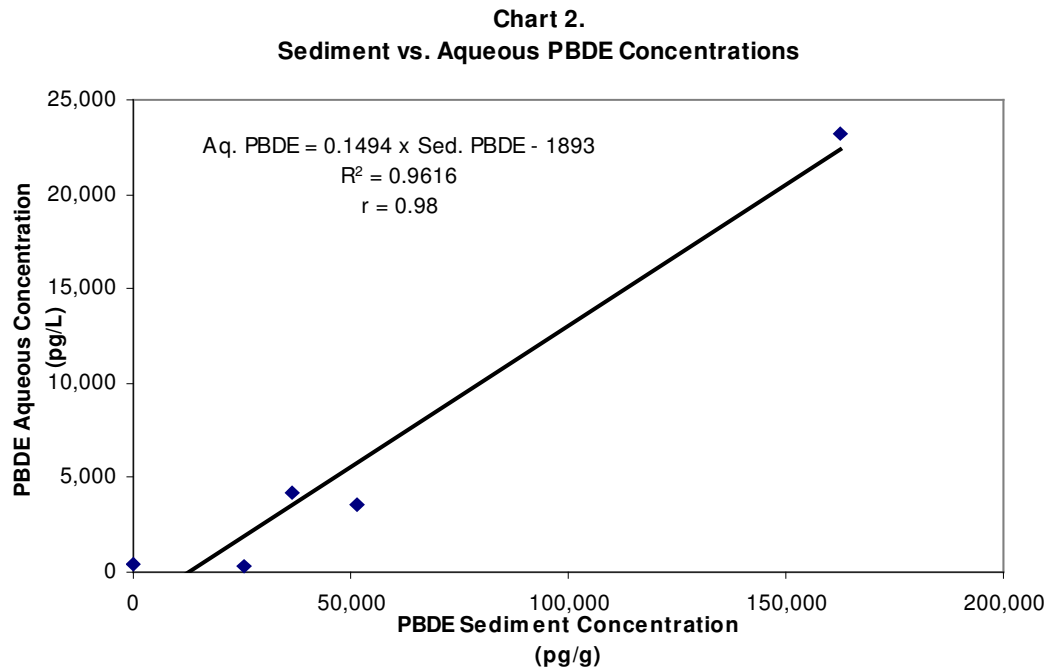
The total sediment PBDE concentration at Irwin Drain (n24) was 162602 pg/g. This was more than three times the next highest total sediment PBDE concentration, 51470 pg/g at Milk River (n1) (Chart 1).



The total sediment PBDE concentration (162602 pg/g) at Irwin Drain (n24) is comparable to the total PBDE concentration found in the sludge at the Palo Alto, CA wastewater treatment plant (61 to 1440 µg/kg). The total aqueous PBDE concentration at this site is also comparable to that found in the liquid effluent from that plant (4 to 29000 pg/L) [7].

It also seems noteworthy that no PBDEs were recovered from the Clinton River (n23) sediment sample, and only 450 pg/L PBDEs were recovered from the aqueous sample taken at this site.

Another noteworthy observation is the high correlation ($r = 0.98$) between the aqueous and sediment PBDE levels found in this project (Chart 2).



Finally, the concentrations of PBDEs found in the fish tissue homogenates (4350 pg/g for the Carp homogenate and 18843 pg/g for the Northern Pike homogenate) agree rather well with the values for Columbia River Whitefish (4.5 - 19.1 ng/g) obtained by Ikonomou in the Columbia River study [8]. However, the relative concentrations of PBDEs in benthic (Carp) versus pelagic (Northern Pike) fish homogenates were opposite those found by Letcher in the Detroit River project (2906 pg/g for Carp and 942 pg/g for Northern Pike) [6].

Acknowledgements:

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